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PATENT SPECIFICATION

NO DRAWINGS

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885,523

Date of Application and filing Complete Specification: Dec 8, 1958.

No. 39505/58.

Complete Specification Published: Dec. 28, 1961.

Index at acceptance:—Classes 2(3), C2B40(A: C: J2: K); 2(2), A2, E(1B: 6D1); 2(5), R33P; 2(6), P2A, P2D1(A: B), P2K7, P2T2(A: X), P7A, P7D(1B: 1X: 2A1), P7K2, P7T2(A: X); and 140, P3(E: F2: F5: G4).

International Classification:—C07c. C08b, f, g. D06m.

COMPLETE SPECIFICATION

Isocyanato-Urethane Waterproofing Agents and Materials Waterproofed therewith

We, ESSO RESEARCH AND ENGINEERING COMPANY, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new waterproofing agents and to textile fibers or goods treated therewith. In a preferred aspect it relates to monoadducts of long-chain hydroxylated hydrocarbons with aromatic diisocyanates and the use of these products as waterproofing agents for materials containing active hydrogens, especially cellulosic materials. Particularly effective embodiments of this invention relate to waterproofing agents derived by reaction of a hexadecyl alcohol or of hydroxymethylated butyl rubber with tolylene diisocyanate or the like.

The invention is applicable to fabrics, fibers or materials that contain active hydrogens, especially cellulosic or polysaccharide-containing materials such as cotton fibers or fabrics, paper products, regenerated cellulose filaments or films made of viscose, cellulose acetate, or the like, substituted cellulose ester or ether filaments in which at least some of the hydroxyl groups of the cellulose remain unsubstituted. Nitrogen-containing fibres may also be treated in accordance with the invention, e.g. protein-containing textile materials such as wool and silk fibers and polyamide fibers such as nylon.

It is broadly known that materials or fibers of the aforementioned types can be made waterproof by chemically attaching thereto a hydrophobic group, desirably in such a manner that the strength of the fibers is not impaired thereby. A wide variety of waterproofing materials has been previously proposed for this purpose, including a limited number of monoisocyanates. However, these materials were relatively expensive, usually of relatively low molecular weight and, due to the relatively complex synthesis required, they were available in only a limited number of types.

It has now been discovered that an unusually effective and economically attractive class of waterproofing agents can be made from relatively inexpensive diisocyanates in the form of monourethane adducts of an aliphatic monohydric alcohol containing at least 10 carbon atoms with the diisocyanates. These monourethane adducts may be represented by the formula

$$OCN.R^1.NH.CO.OR,$$

where R is the residue of the monohydric aliphatic alcohol and R^1 is a divalent C_{6-12} hydrocarbon radical. The group R is an aliphatic group consisting predominantly or essentially of carbon and hydrogen atoms, but which may contain one or more oxygen linkages interrupting the carbon chain, and which is hydrophobic in character.

A second and similar class of hydrogen adducts which have been found useful as waterproofing agents in accordance with the invention are the adducts of a hydroxymethylated high molecular weight low-unsaturation hydrocarbon polymer as hereinafter defined, containing from 1 to 10 hydroxy groups per thousand carbon atoms with the diisocyanate, said adduct being essentially a monoisocyanate adduct, i.e. adducts of one diisocyanate molecule with each hydroxy group in the polymer molecule. These polymer adducts consist of a hydrocarbon polymer chain having side groups of the formula

$$OCN.R^1.NH.CO.OCH_2—$$

[*Price 4s. 6d.*]

in the proportion of from 1 to 10 per 1000 carbon atoms in the original polymer.

A highly effective agent of this second class of adducts can be prepared by using slightly hydroxymethylated butyl rubber. Butyl rubber, as is well known, is a copolymer of about 0.5 to 10 weight per cent of a C_4 to C_5 conjugated diolefin, preferably about 2% isoprene, and correspondingly 90 to 99.5 weight per cent of isobutylene, prepared at temperatures below —40° C. in the presence of aluminium chloride or similar Friedel-Crafts catalyst in accordance with the procedure described in U.K. Patent No. 565974. For the purposes of this invention this rubbery copolymer is hydroxymethylated so as to contain from 0.1 to 1.0% of hydroxyl groups, i.e., from 1 hydroxyl group per approximately 100 carbons to 1 hydroxyl group per approximately 1000 carbons. Preferably the hydroxyl groups are introduced by hydroxymethylating the polymer by the Prins reaction.

The "low-unsaturation" hydrocarbon polymers used in the invention are those having an unsaturation of 10 mole % or less. The term "mole % unsaturation" designates the amount of double bonds contained in the polymer. For example, a homopolymer of butadiene which is formed by 1,4 addition of the butadiene molecules has one double bond per unit and by definition such a polymer has 100 mole % unsaturation. Similarly, a polymer of 10% isoprene and 90% isobutylene has theoretically 10 mole % unsaturation because 10% of its composition contains a double bond formed by 1,4-addition of the isoprene molecule.

More unsaturated hydrocarbons such as natural rubber are undesirable for the present purposes, both because they tend to form undesirable gels during the Prins reaction and especially because the resulting products tend to degrade rather rapidly when exposed to air and light.

The Prins reaction is carried out in a manner otherwise well known in the art. For example, the butyl rubber to be hydroxymethylated is dissolved to a concentration of 5—25% by wt. (e.g. 10%) in an inert solvent such as a hydrocarbon or halogenated hydro-carbon, preferably chloroform. To this solution is added 1—10% by wt. (based on polymer) of an acid, preferably a Lewis type acid, e.g. 5% of boron trifluoride etherate, together with 1—10% by wt. (based on polymer), preferably about 5% of paraformaldehyde, the reaction is allowed to proceed for 1—24 hours at a temperature of 0°—100° C., preferably about 10 hours at 20°—40° C. The product may be recovered as a solution by washing the reaction mixture with 1—10% aqueous sodium hydroxide solution followed by water. Or the solid polymer may be recovered by precipitation. Precipitation is accomplished by the addition to the polymer solution of 0.5—10 parts of a solvent in which the polymer is insoluble, e.g. the lower oxygenated compounds, preferably containing 1—4 carbon atoms and preferably being either an alcohol such as isopropanol or a ketone such as methyl ethyl ketone. If desired a combination of precipitation and washing may be used for product recovery.

In preparing the adducts, the hydroxy compound is suitably reacted with the diisocyanate in the amount of at least one molecule per hydroxyl group in the hydroxy compound. However, at least a 20 mole per cent excess of diisocyanate is preferred since this tends to favor the formation of the monoadduct (isocyanato monourethane) and repress the formation of the unwanted diadduct (diurethane). It will be realised that, when using the hydroxymethylated polymer reactant, the resultant adduct may contain a plurality of diisocyanate units per molecule depending on the number of hydroxyl groups present in the starting polymer molecules. In the sense that, in these polymer adducts, according to the invention, each diisocyanate molecule reacts with only one hydroxyl group the adducts are still mono-adducts and this latter and similar terms are to be construed accordingly. At about diisocyanate/hydroxyl compound mole ratios of about 1.3 or greater, the hydroxyl compound can be essentially completely converted to the mono-adduct. Aromatic diisocyanates, and more especially tolylene 2,4-diisocyanate or a commercial mixture of tolylene diisocyanate isomers are particularly useful. However, other suitable diisocyanates include p-phenylene diisocyanates, xylylene diisocyanates, as well as aliphatic diisocyanates such as 1,6-hexamethylene diisocyanate. Generically, these compounds may be described by the formula OCN—R^1—NCO wherein R^1 is a divalent aliphatic, alicyclic or aromatic radical of 6 to 12 carbon atoms. Aromatic diisocyanates of the above formula, wherein R^1 is a divalent aromatic radical of 6 to 8 carbon atoms and wherein the isocyanate groups are in meta position with respect to each other, and aliphatic diisocyanates containing the isocyanate groups attached to the terminal carbon atoms of the hydrocarbon radical are particularly suitable.

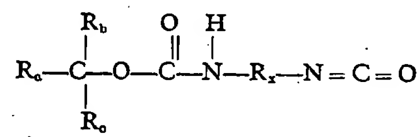
The required adduct formation is preferably carried out by dissolving the hydroxy compound in a suitable inert solvent containing no active hydrogen such as pentane, hexane, heptane, cyclohexane, benzene, toluene, and halogenated hydrocarbons. Concentrations of such solutions may range between about 1 to 40% by wt., of polymer, preferably 10—30% i.e. the solutions are prepared in sufficiently fluid form to permit effective stirring and mixing. When the solution is mixed with the diisocyanate, the reaction proceeds spontaneously and fairly rapidly even at room temperature. Suitable reaction temperatures are in the range between 0°—100° C., preferably 20°—80° C. The reaction is desirably carried out in

an inert atmosphere, e.g. nitrogen, in order to avoid reaction of the isocyanate groups with oxygen or moisture. Yields equal or close to 100%, based on the hydroxy compound, can be obtained. The remaining excess unreacted isocyanate can be removed from the reaction mixture by distillation.

A wide variety of hydroxy compounds are useful in making the isocyanatourethanes of this invention. A particularly useful class consists of C_{10-30}, especially C_{10-14} alkanols. Another useful class consists of C_{10-30} alkoxy-alkanols which contain from 5 to 15, and preferably at least 8, carbon atoms in each of the two alkyl portions. Besides these preferred groups of aliphatic monohydric alcohols many other aliphatic monohydric alcohols containing as many as several hundred carbon atoms per molecule may be used. The carbon atoms may be arranged in the form of an uninterrupted straight or branched carbon chain, or the carbon chain may be interrupted by oxygen linkages at intervals of preferably not less than 10 carbon atoms. Examples of suitable alkanols include decanols, hexadecanols, eicosanols. tricontanols, etc. These can be prepared in various ways. For instance, carbonylation of olefins in the presence of a cobalt catalyst and hydrogenation of the resulting aldehyde as described in U.S. Patent 2,327,066 produces branched chain alcohols generally referred to as Oxo alcohols. The dimeric alcohols usually found in Oxo bottoms and containing an ether linkage can also be used. An example of such an alcohol is the dimeric alkoxy alcohol $C_{10}H_{21}O.C_{11}H_{22}OH$, found in C_{10} Oxo alcohol bottoms. Aldox type dimer alcohols resulting from aldol condensations in the Oxo process are similarly useful. Straight chain alcohols of suitable molecular weight can be prepared by the Ziegler process wherein an olefin such as ethylene or propylene is polymerized to the desired molecular weight in the presence of an aluminium alkyl catalyst such as aluminum triethyl to give the corresponding long chain aluminium alkyl and the latter is finally hydrolyzed to give the desired alcohol as described, for instance, in Belgian Patent 540,198. Other useful alcohols such as aluryl or stearyl alcohols can be obtained from natural products, e.g. from fats, or by polymerizing ethylene in an alcohol solution with the aid of a peroxide catalyst.

Another important class of useful hydroxy-compounds consists of suitably hydroxymethylated rubbery or resinous polymers of low unsaturation of 10 mole % or less, such as butyl rubber, petroleum resins (e.g. those having a molecular weight of about 1000 and prepared from a steam cracked C_5—C_7 hydrocarbon stream according to U.K. Patent 743,886), polypropylene from Friedel-Crafts polymerization, styrene-diolefin copolymers such as those prepared by copolymerizing a small amount of butadiene-1,3 with styrene in aqueous emulsion in the presence of a peroxy catalyst.

The preferred alcohol adducts of this invention can be represented by the following formula:—



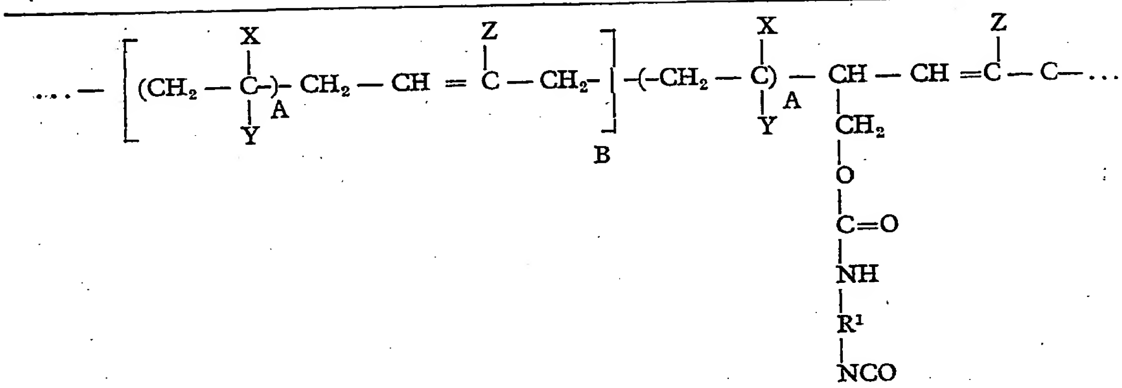
wherein:—

R_a is an aliphatic radical containing 9 to 200 or more carbon atoms either in the form of a straight or branched uninterrupted hydrocarbon chain or in the form of a plurality of oxygen-linked hydrocarbon chains of at least 9 carbon atoms each,

R_b and R_c are hydrogen or C_{1-10} alkyl radicals, and

R_x is a divalent aliphatic or aromatic radical of 6 to 12 carbon atoms, e.g. 2,4-tolylene.

In the case of high molecular weight olefin-diene copolymers such as butyl rubber, a segment of the adducts based thereon can be pictured as follows:



wherein:

R = divalent alkyl or aryl radical of 6 or more carbon atoms

X = H, CH_3, C_2H_5, C_3H_7, phenyl, etc.

Y = H, CH_3, C_2H_5, etc.

Z = H, CH_3, C_2H_5, etc.

A = 1 to several hundred

B = 1 to 100

it being provided that the total of A + B is sufficient to satisfy the requirement that the adduct contains from 1 to 10 isocyanato side groups per 1000 carbon atoms of the original polymer.

For instance, when the waterproofing agent is prepared from butyl rubber containing 2 mole per cent polymerized isoprene of which 1 isoprene unit in 10 has been hydroxymethylated and reacted with tolylene diiso-cyanate, X, Y, and Z in the above formula represent methyl groups, R[1] represents tolylene, A may equal 49 and B may equal 9.

Characteristically, all the products of this invention contain at least one long aliphatic hydrophobic chain and, for all practical purposes only one isocyanate group per molecule or large polymer segment. They are clearly distinct from previously known isocyanate derivatives which have molecules possessing relatively short hydrocarbon portions and many isocyanate groups per molecule, as described, for instance, in U.S. Patent 2,537,064. The latter agents not only require a rather complex synthesis but, due to the many isocyanate groups present per molecule, cause profuse cross-linking and consequently some stiffening of fibers when reacted therewith in sufficiently great proportion. They have accordingly been used for imparting crease resistance to fabrics, but have been relatively ineffective as waterproofing agents. By contrast, the hydrophobic monoisocyanate compounds of the present invention impart outstanding water resistance to fabrics even when used in very minute concentrations without, however, causing any significant cross-linking or immobilization of the treated fibers.

After completion of the adduct forming reaction, the resulting reaction mixture is usually too concentrated for direct use in impregnation. Consequently, it is desirably diluted with additional solvent to form a solution containing about 0.2 to 5% by wt., preferably about 0.5 to 2% of the adduct. This solution is then used for treating the textile or other material to be waterproofed, e.g., by refluxing or merely by dipping to impregnate the material with the solution followed only by drying or baking in an oven. Depending on the boiling point of the refluxing solvent, the temperature of this treating step may be between 30° to 150° C. and below the softening point of the material. It is desirable to treat the active-hydrogen containing fibers or films with sufficient treating solution and for a sufficient time to incorporate therein 0.1 to 1.0 wt. %, preferably 0.1 to 0.5 wt. %, of the isocyanato urethane adduct in the case of alcohol adducts and 0.1 to 10 wt. %, preferably 1 to 10 wt. % in the case of the high molecular weight hydroxymethylated polymer adducts. Due to the high proportion of the hydrophobic part to the rest of the molecule in the case of the high molecular weight polymer adducts, a thicker layer thereof is generally combined with the material to be

treated than when a relatively low molecular weight alcohol adduct is used.

In carrying out the impregnation it is convenient to have at least about 0.1 to 10 parts by wt. of adduct present and thus available for reaction in the treating solution per 100 parts by wt. of cellulosic or other material being treated. After completion of the treatment, the solution is drained off and the material dried, e.g., at 30° to 150° C. If desired, any unreacted diisocyanate and adduct which are deposited but not chemically bound to the material may be removed from the impregnated material by extraction with a hydrocarbon.

Since the novel treating agents are attached to the substratum in the form of a thin, presumably monomolecular layer, the treatment has no noticeable effect on the appearance or feel of the material treated. However, the material is made essentially impervious to water. Once the adduct has been properly reacted with the fibers, its effect is essentially permanent since it is not washed out either by laundering or dry cleaning.

For a better understanding, the invention will now be illustrated by actual working examples. Unless otherwise indicated, all proportions of materials are expressed on a weight basis.

EXAMPLE 1

A solution of 159.8 g. (0.915 mole) of freshly distilled 2,4-tolylene diisocyanate (BP 122°—145° C. at 15 mm.) was made in 75 cc of dry hexane. This solution was placed in a glass reaction flask equipped with a dropping funnel and a stirrer. Another solution of 72.6 g. (0.3 mole) of C_{17} alkoxyl alcohol ($C_8H_{17}O.C_9H_{18}OH$ from C_8 Oxo bottoms) was made in 75 cc of dry hexane.

The second solution was added to the first in increments over a period of 105 minutes with stirring. During this time the temperature of the reaction mixture had risen from 24.5° C. to 45.5° C. The mixture was then refluxed for ½ hr. to complete the reaction.

A still head was attached to the reaction vessel and the distillable material removed. The product boiling above hexane was taken as three cuts.

(A) 101.0 g. B.P. 130° C. (15 mm)
—95.0° C. (1.0 mm)
(B) 29.5 g. B.P. 102° C. (1.0 mm)
—165° C. (1.0 mm)
(C) 109.0 g. non-volatile product (viscous oil)
Total
Recovery 239.5 g. = 98.5%

The non-volatile product is the alcohol-diisocyanate adduct and amounts to 90.5% of theoretical yield. In attempting to distill this product the excessively high pot temperature of 237° C. was reached. It was observed that some decomposition to volatile products (presumably reversal of the reaction) occurred. In the absence of such drastic treatment even higher yields of the adduct can be isolated.

EXAMPLE 2

Sizing agents were removed from a piece of white Indian-head cotton by alternate washing with aqueous soap solution and extraction with a light naphtha hydrocarbon solvent. A sample of the resulting cloth weighing 6.8 g. was treated with a refluxing solution of 1.5 g. of the adduct of Example 1 in 150 cc of heptane for 2.5 hours. The cloth was then squeezed and washed in fresh n-heptane twice; then refluxed in fresh heptane for 5 minutes to remove any unreacted adduct. After drying in an oven at 140° F. and standing in the air to equilibrate with atmospheric moisture, the sample actually weighed less than the original untreated cloth. This loss in weight is due to the fact that the treated cloth is quite hydrophobic and consequently takes up much less moisture than the untreated cloth. The appearance of the sample was not altered but the cloth was now quite waterproof. Tensile tests, summarized below, showed that the strength of the cloth had not been impaired.

STRENGTHS OF 1/2″ STRIPS OF CLOTH (CUT PERPENDICULAR TO SELVAGE) RUN ON A SCOTT TESTER:

	Untreated Cloth lbs./1/2″ Strip	Treated Cloth lbs./1/2″ Strip
#1	38.0	43.0
#2	41.5	39.0
#3	42.0	41.5
Average	40.5	41.2

EXAMPLE 3

An absorbent paper towel was saturated with a 1% solution of the adduct of Example 1 in n-heptane. The towel was then dried in an oven at 140° F. for ½ hour. It was then found to be impervious to a stream of water from a faucet.

EXAMPLE 4

In this test the hexane solvent was dried by distillation of a portion thereof and discarding. Likewise the apparatus was dried by distillation of hexane.

158.8 g. (.91 mole) of freshly distilled commercial tolylene diisocyanate (B.P. 93°—119° C. at 3 mm.) was placed in a 500 cc. 3-neck flask equipped with a stirrer. To this mixture was added dropwise with stirring over a period of 43 minutes a solution of 60 g. (0.30 mole) of a tridecanol (C_{13} Oxo alcohol) in 75 cc. of n-hexane. During this period the pot temperature had risen spontaneously from 22.5° C. to 45.0° C. The mixture was then refluxed for 105 minutes to complete reaction.

A stillhead was attached to the reaction vessel and, after removal of the hexane, the product separated into two fractions: (A) the recovered excess diisocyanate and (B) the non-volatile adduct.

(A) 107.6 g.	B.P. 84°C. (1.4 mm.)—122°C. (0.3 mm.)
(B) 111.0 g.	(non-volatile at pot temp. 195°C. at 0.3 mm.)
218.6 g.	recovery = 99.9%
Yield of (B) = (Viscous oil)	99% of theory.

EXAMPLE 5

8.3 g. of the adduct prepared in Example 4 was dissolved in sufficient n-heptane to make 1 liter of solution. A piece of dry white Indian-head cotton from which the sizing agents had been removed as described before, and which weighed 10.754 g., was saturated with 14 cc. of this solution. The amount of adduct thus available to react with the cloth was 0.116 g. or 1.08 wt. % on cloth. The cloth was baked in an oven at 200° F. for 2 hrs. It was then extracted twice with normal heptane to remove any unreacted adduct and dried in the oven for 20 minutes. After coming to equilibrium with atmospheric moisture the piece of cloth weighed 10.783 g., a gain of 0.29 wt. %. The cloth was unchanged in appearance but was quite waterproof: when cupped so as to form a bag and filled with tap water no penetration of water occurred. The strength of the cloth was not adversely affected by this treatment as shown below.

POUNDS OF BREAKING STRENGTH OF 1/2" WIDE STRIPS OF CLOTH DETERMINED ON SCOTT TESTER:

		Untreated Cloth	Treated Cloth
Parallel to selvage		39.0	46.0
		47.0	50.5
		53.5	—
	Ave.	46.5	48.3
Perpendicular to selvage		36.2	42.0
		40.0	41.2
		43.0	47.0
		40.8	39.0
		46.5	40.0
	Ave.	41.3	41.8

EXAMPLE 6

A solution of the adduct prepared in Example 4 was made in heptane so as to contain 2.1 mg. of adduct per cc of solution. A double sheet of newspaper weighing 25.5 g. was saturated with 40 cc of this solution. Thus 84 mg. or 0.33 wt. % of adduct was made available for reaction with the paper. The paper was baked in an oven at 200° F. for 10 minutes. There was no change in appearance.

This treatment imparted a considerable degree of water resistance. When held folded

under a fast running faucet the water did not soak through the top sheet and this sheet was essentially dry in 10 minutes exposure to air. A similar treatment of a piece of untreated paper caused soaking through 3 sheets which were not dry even in an hour.

EXAMPLE 7

Formation of adduct of tolylene diisocyanate with hydroxy-methylated butyl rubber:

Butyl rubber (Enjay Grade 325) containing 2% of combined isoprene was hydroxy-methylated by the Prins reaction so as to contain about 0.4 wt. % hydroxyl groups as determined by the infrared spectrum. The hydroxymethylation was carried out as follows:

100 gm. of the butyl rubber dissolved in 850 cc. chloroform was charged to a 3-neck flask fitted with a stirrer and a dropping funnel. A complex, made by heating 5.3 gm. of boron tri-fluoride etherate, 3.2 gm. paraformaldehyde and 50 cc. chloroform, was added with stirring under nitrogen. The total mixture was stirred at room temperature for 7 hrs. under nitrogen and allowed to stand overnight. The resulting modified butyl rubber was precipitated with acetone and redissolved in hexane. The hexane solution of modified rubber was then washed with 5% aqueous sodium hydroxide solution, then with water until neutral to litmus, and the rubber precipitated with acetone. The modified rubber was finally dried for 22 hrs. at 60° C. and 20 inches vacuum. In appearance it was indistinguishable from the initial unmodified polymer. As a test, five drops of tolylene diisocyanate were added to a solution of 2 gms. of the modified rubber in hexane. The mixture gelled overnight indicating the presence of hydroxyl groups. Infrared analysis indicated 0.4 wt. % hydroxyl on the rubber.

To a three-neck flask fitted with a dropping funnel and a stirrer was charged 101.9 g. of 20 wt. % hydroxy-methylated butyl rubber in hexane. To this was added 1.5 g. (.0086 mole) of a commercial mixture of tolylene diisocyanate isomers in 15 cc of hexane. The resulting mixture was stirred for 1 hour under nitrogen. Then 0.5 g. (0.002 mole) of a hexadecanol (C_{16} Oxo alcohol) in 15 cc of hexane was added and the mixture stirred under nitrogen for 1 hour to react with excess diisocyanate. The final concentration of butyl adduct was 18.3 wt. %.

EXAMPLE 8

A sample of white Indianhead cotton, with sizing removed, was refluxed for two hours in a hexane solution of the butyl rubber adduct described in Example 7. The cloth was then exhaustively extracted 5 times with hexane to remove any rubber that was not chemically bound to the cloth, then dried 1 hour in an oven at 180°F. The weight of cloth before treatment was 6.908 g. and after treatment 7.163 g. The amount of rubber chemically attached was 3.7 wt. %. The treated cloth had the same strength as untreated cloth as determined on a Scott tester. The cloth was not penetrated by water standing on the cloth for six days.

A similar piece of cloth was treated under the same conditions with a solution of unmodified "Enjay 325" butyl rubber in hexane. After extraction with hexane the gain in weight was 0.3% and the sample was not waterproof.

EXAMPLE 9

A. A solution of 65.5 gm. (0.376 mole) of freshly distilled tolylene diisocyanate in 75 cc sodium-dried hexane was charged to a 3-neck flask fitted with a stirrer, a dropping funnel and a reflux condenser. A solution of 726 gm. (0.3 mole) of a C_{16} monohydric Aldox alcohol ($C_{16}H_{33}OH$) in 75 cc dry hexane was added to this with stirring under nitrogen. Addition required 35 minutes during which interval the temperature rose from 21°C. to 49°C. The mixture was then refluxed 40 minutes. The hexane was stripped out and the excess tolylene diisocyanate was distilled at 1.1 mm. pressure until the pot temperature reached 195°C. The yield of non-volatile product was 124.1 gm., which corresponds to a yield of 97.3% of the monoadduct and 2.7% of the diadduct.

B. Similar preparations were made but with different molar ratios of tolylene diisocyanate (TDIC) to alcohol. The corresponding yields of monoadduct are summarized in Table I.

TABLE I

EFFECT OF REAGENT PROPORTIONS ON MONOADDUCT YIELD

TDIC/Alcohol Mole Ratio	Monoadduct Yield Wt. % (on alcohol)
1.0	62
1.05	79
1.15	89.5
1.2	91.5
1.25	97.5
1.5	99.5

From the above data it is apparent that at TDIC/alcohol mole ratios of at least 1.2, better than 90% yields of the desired isocyanourethane monoadduct are obtained, whereas at lower ratios the formation of the unwanted diadduct (diurethane) increases rather abruptly. The diurethane, of course, is incapable of reacting with cotton fibers or the like. For this reason it is most desirable to carry out the reaction at diisocyanate/alcohol mole ratios between about 1.2 and 2, preferably between 1.25 and 1.5 in which range virtually perfect selectivity to the monoadduct is attained. However, the preferred ratio may vary somewhat depending on the specific reagents employed.

Wool suiting is rendered waterproof when impregnated with a hexane solution containing 0.5% of the product of Example 9A (in an amount providing 1.6 weight percent available for reaction per weight of fabric) and baked in an oven for 90 minutes at 80°C. The treated cloth in not wet or penetrated by water.

EXAMPLE 10

To a solution of 65.3 g. (0.375 mole) of tolylene diisocyanate in 75 cc of dry hexane was added over a period of 40 minutes a solution of 93.6 g. (0.329 mole) of a C_{21} alkoxy alcohol ($C_{10}H_{21}OC_{11}H_{22}OH$). The temperature of the reaction mixture rose spontaneously from 25°C. to 42°C. over the course of the addition. The mixture was refluxed 1.5 hours to complete the reaction and the hexane then removed by distillation. A volatile cut amounting to 11.9 g. (B.P. 87°—116°C. at 1.1—1.9 mm.) was then removed by distilling to a pot temperature of 183°C. A non-volatile residue of 142.2 g. remained. This corresponds to a yield of 96.3% of theory of the alcohol-diisocyanate monoadduct and 3.7% of the diadduct.

Nylon cloth is made waterproof when treated with a dilute heptane solution of the above adduct to make 0.8 weight percent of the adduct (based on cloth weight) available for reaction, followed by baking for 1 hour at 70°C.

The adducts of Examples 4, 9 and 10, all of which were viscous oils, have been found to have the characteristics summarized in Table II.

TABLE II

MONO ADDUCTS OF THE INDICATED ALCOHOLS WITH TOLYLENE DIISOCYANATE

Example	4	9	10
Alcohol Reagent	C_{13} Oxo Alcohol	C_{16} Aldox Alcohol	C_{21} Alkoxy Alcohol from C_{10} Oxo bottoms
d_4^{25}	1.0261	1.0079	0.9868
n_D^{25}	1.5168	1.5120	1.5015
% Carbon			
Found	70.20 70.97	72.48	71.68
Theory	70.55	72.08	71.67
% Hydrogen			
Found	9.08 9.41	9.98	9.88
Theory	9.16	9.67	10.03

WHAT WE CLAIM IS:—

1. A process for the preparation of isocyanato-urethane compounds which comprises reacting a diisocyanate of the formula OCN.R¹.NCO, wherein R¹ is a divalent C_{6-12} hydrocarbon radical, with an aliphatic monohydroxy alcohol containing at least 10 carbon atoms or a hydroxymethylated high molecular weight low-unsaturation hydrocarbon polymer, as hereinbefore defined, containing from 1 to 10 hydroxy groups per thousand carbon atoms, to produce a monoisocyanate, as hereinbefore defined, adduct.

2. A process according to Claim 1, wherein the diisocyanate reactant is used in a proportion of at least one molecule per hydroxyl group in the hydroxy reactant.

3. A process according to Claim 2, wherein the diisocyanate reactant is used in a proportion of from 1.2 to 2 molecules per hydroxyl

group in the hydroxy reactant.

4. A process according to Claim 1, 2 or 3, wherein the reaction is carried out at a temperature of from 0° to 100°C.

5. A process according to any one of the preceding claims, wherein the diisocyanate is tolylene diisocyanate.

6. A process according to any one of the preceding claims, wherein the hydroxy compound is an alkanol of 10 to 30 carbon atoms.

7. A process according to any one of Claims 1—5, wherein the hydroxy-compound is an alkoxy alkanol containing from 5—15 carbon atoms per alkyl group.

8. A process according to any one of Claims 1—5, wherein the hydroxy-compound is hydroxymethplated butyl rubber containing from 1 to 10 hydroxyl groups per 1000 carbon atoms.

9. A process according to any one of the preceding claims, when carried out in a solvent containing no active hydrogen.

10. A process according to any one of the preceding claims, when carried out in an inert atmosphere.

11. A process according to Claim 1, when carried out substantially as hereinbefore described in any one of Examples 1, 4, 7, 9 and 10.

12. Monoisocyanate adducts, as hereinbefore defined, when prepared by a process claimed in any one of the preceding claims.

13. An isocyanatourethane compound of the formula OCN.R[1].NH.CO.OR wherein R^1 is a divalent C_{6-12} hydrocarbon radical and R is a hydrophobic aliphatic radical containing at least 10 carbon atoms.

14. A compound according to Claim 13, wherein R^1 is a divalent aromatic radical of 6 to 8 carbon atoms and wherein the isocyanate and urethane groups are attached thereto in metal positions with respect to each other.

15. A compound according to Claim 14, wherein R^1 is 2,4-tolylene.

16. A compound according to Claim 13, wherein R^1 is 1,6-hexamethylene.

17. A compound according to any one of Claims 13—16, wherein R is a C_{10-30} alkyl group or a dialkyl ether radical containing 5—15 carbon atoms in each alkyl group.

18. A compound according to any one of Claims 13—16, wherein R is a C_{10-18} alkyl group.

19. A compound according to any one of Claims 13—16, wherein R is a dialkyl ether radical containing at least 8 carbon atoms in each alkyl group but not more than a total of 30 carbon atoms.

20. An adduct, being a monoisocyanate adduct as hereinbefore defined, of a hydroxymethylated high molecular weight low-unsaturation hydrocarbon polymer, as hereinbefore defined, containing from 1 to 10 hydroxy groups per 1000 carbon atoms with a diisocyanate of the formula OCN.R[1].NCO, where R^1 is a divalent C_{6-12} hydrocarbon radical.

21. An adduct according to Claim 20, which is an adduct of a hydroxymethylated rubbery copolymer of 90—99.5% by weight isobutyene and 10—0.5% isoprene, with the said diisocyanate.

22. An adduct according to Claim 20 or 21, which is an adduct of an isocyanate of the formula OCN.R[1].NCO where R^1 represents a divalent C_{6-8} aromatic radical having the isocyanate groups attached thereto in meta position with respect to each other.

23. An adduct according to Claim 22, wherein R^1 represents a 2,4-tolylene radical.

24. A process which comprises treating a fibrous material containing active hydrogen atoms with a compound claimed in any one of Claims 12—23.

25. A process according to Claim 24, which comprises impregnating the fibrous material with a solution containing from 0.2 to 5% by weight of said compound.

26. A process according to Claim 25, which comprises impregnating the fibrous material with a solution containing from 0.5 to 2% by weight of said compound.

27. A process according to Claim 25 or 26, in which the impregnating step is carried out at a temperature of from 30° to 150°C.

28. A process according to Claim 25, 26 or 27, which comprises treating the fibrous material with a solution of a compound as claimed in any one of Claims 13—19 for sufficient time to incorporate therein from 0.1 to 1.0% by weight of the adduct.

29. A process according to Claim 25, 26 or 27, which comprises treating the fibrous material with a solution of a compound as claimed in any one of Claims 20—23 for sufficient time to incorporate therein from 0.1 to 10% by weight of the adduct.

30. A process according to any one of Claims 24—29 in which the fibrous material treated comprises nitrogen-containing fibres.

31. A process according to any one of Claims 24—29, in which the fibrous material treated comprises polysaccharide fibres.

32. A process according to Claim 24, when carried out substantially as hereinbefore described in any one of Examples 2, 3, 5, 6, 8, 9 and 10.

33. Fibrous materials when treated by a process claimed in any one of Claims 24—32.

34. An active hydrogen-containing fibrous material impregnated and chemically bonded with a compound claimed in any one of Claims 12—23.

35. A fibrous material according to Claim 34, impregnated and chemically bonded with from 0.1 to 1.0% by weight of a compound claimed in any one of Claims 13—19.

36. A fibrous material according to Claim 34, impregnated and chemically bonded with

from 0.1 to 10% by weight of an adduct as claimed in any one of Claims 20—23.

37. A fibrous material according to any one of Claims 34—36 which comprises polysaccharide fibres.

38. A fibrous material according to any one of Claims 34—36 which comprises nitrogen-containing fibres.

39. A fibrous material according to any one of Claims 34—39 which is a textile material.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1961.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.